

# CHEMICAL LAWS:

A SUPPLEMENT

TO

GOODWIN'S

TEXT BOOK OF CHEMISTRY

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## PREFACE.

IN the following pages the principal chemical laws are developed independently of theories. Doubtless the mental bias consequent upon the habitual use of theory will appear here and there. In the writer's teaching experience he has found that when chemical laws are presented in the usual way along with chemical theories, there commonly results a wrong idea of their relations. The principal object of this short treatise is to emphasise the truth that chemical laws are generalisations from facts, and can be considered apart from theory.

W. L. GOODWIN.

QUEEN'S UNIVERSITY,  
Kingston, Ont., March 29th, 1893.

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## CHEMICAL LAWS.

1. A **Chemical species** includes all portions of the same kind of homogeneous substance. Pure salt, sugar, water, gold, iron, and oxygen are examples of chemical species. When a substance crystallises, the crystals are the *individuals* of the species. Chemical species are either *elements* or *compounds*. When substances undergo such a change that they disappear and become other species of substance, a *chemical change*, or *chemical action*, has taken place. Chemical changes are of several kinds:—

(1) **COMBINATION**.—Two or more substances (chemical species) combine to form one.

(2) **SIMPLE DECOMPOSITION**.—One substance (species) gives rise to two or more different substances (species).

(3) **DOUBLE DECOMPOSITION or METATHESIS**.—Two substances exchange one or more of their elements, so as to form two new substances.

(4) **REPLACEMENT or SUBSTITUTION**.—One species replaces one or more constituents of another. This replacement may be accompanied by the union of another portion of the replacing species with the replaced, as when chlorine replaces hydrogen in hydrocarbons. It not only takes the place of the hydrogen, but also forms a compound, hydrochloric acid, with the replaced hydrogen. This kind of change has been called *metalepsis*.

(5) **ISOMERIC CHANGE\***.—One species becomes changed

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\* *isos*, equal : *meros*, part.

into one other of the same composition but different properties. Thus under certain conditions *acetylene* (carbon, 92.3%; hydrogen, 7.7%) becomes changed into *benzene* (same composition), a substance different in its properties. *Ammonium cyanate* (nitrogen, 46.67%; hydrogen, 6.66%; carbon, 20%; oxygen, 26.67%) becomes *urea*, a substance of exactly the same composition, but quite different in properties. This phenomenon, at first sight very hard to explain, admits of easy explanation by the modern chemical theory.

Changes in colour, smell, taste, physical state, crystalline form, density, solubility, melting point, boiling point, and other properties are accompaniments of chemical change; but the most constant characteristic is the appearance or disappearance of sensible heat.

**2. The Law of Combining Proportions.**—A study of *mass-relations* in chemical change brings out certain laws, which can be included in a general statement, as follows:—

*In every chemical change involving two or more substances, the masses\* of the substances changed are always in the ratio of the combining numbers of the substances, or of simple multiples of them.*

These *combining numbers*, or *combining weights*, are found by studying by means of the balance the proportions in which elements unite to form compounds and the proportions in which compounds react on each other. Thus, *lead* and *oxygen* combine in the proportion of 100 to 7.7 and form *litharge*; *lead* and *sulphur* in the proportion of 100 to 15.4 to form *lead sulphide*; and *sulphur* and

\* Or, practically, the weights.

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oxygen in the proportion of 15.4 to 23.1 (or  $3 \times 7.7$ ) to form *sulphur trioxide*. If 100 be chosen as the combining number for lead, then 7.7 becomes that of oxygen, and 15.4 that of sulphur. But lead forms other compounds with oxygen, in one of which, *lead peroxide*, there are 15.4 parts of oxygen for every 100 of lead. This leads to a doubt as to which number should be chosen for the combining number of oxygen; and the difficulty increases as elements are examined which combine with other elements in a large number of different proportions. It is now the universal practice to refer the combining numbers of the elements to *1 part by weight of hydrogen*; and oxygen must be first examined. But hydrogen forms two compounds with oxygen, *water* (1:8), and *hydrogen peroxide* (1:16). Shall 8 or 16 be taken as the combining number for oxygen? The same difficulty appears when compounds are studied. For example, hydrogen combines with acetylene in two proportions forming *ethylene* (1 of hydrogen to 13 of acetylene) and *ethane* (1 of hydrogen to  $6\frac{1}{2}$  of acetylene); there is thus a choice between 13 and  $6\frac{1}{2}$ . Up to the middle of this century, this difficulty existed and led to great confusion, as different chemists used different combining numbers and employed the same symbols\* to represent them; so that the composition of the same compound was represented by different formulas. Thus,  $\text{Ag}_2\text{O}$ ,  $\text{AgO}$ , and  $\text{AgO}_2$  were all used to indicate a compound composed of silver and oxygen in the proportion of 108 to 8. It is evident that this difficulty could not have been surmounted by mere study of the proportions in which substances react.

\* Symbols are letters chosen to represent the combining weights of the elements. Formulas of compounds are obtained by combining these symbols so as to represent correctly the composition of compounds.

3. **The Law of Gas Density\***.—It is clear, too, that if some systematic way can be found for choosing the combining weights of compounds, the problem will at the same time be solved for elements. For, let there be taken as the combining weight of any element the *smallest* weight of it found in the combining weight of any of its compounds. Now, it has been found that a very simple law connects the physical and chemical properties of gaseous substances. The following table will make clear the nature of this law :—

	I. Specific Weights. (Air=1.)	II.	III. Combining Weights.
Hydrochloric Acid (gas) .....	1.265	36.5	36.5
Water (in the gaseous state)...	0.63	18	9 or 18
Ammonia .....	0.59	17	5 $\frac{1}{2}$ , 11 $\frac{1}{2}$ or 17
Carbon Dioxide .....	1.52	44	22 or 44
Carbon Monoxide .....	0.97	28	14 or 28
Methane .....	0.552	16	8 or 16
Ethane .....	1.04	30	15 or 30
Ethylene .....	0.97	28	14 or 28
Acetylene .....	0.90	26	13 or 26

In order to bring out the relation between these numbers, calculate the specific weights to the same scale as the combining weights. This can be done by taking 36.5 as the specific weight of hydrochloric acid and multiplying all the other numbers in the column by  $\frac{36.5}{1.265}$ . This, of course, preserves the ratio between the specific weights, but refers them to 36.5 of hydrochloric acid instead of 1 of air. These numbers have been placed in column II. of the table. Small fractions are neglected. It is at once evident that, if the right choice is made, *the specific*

\* *Gas Density* is used as a general term for the specific weight of a substance in the gaseous state. It is convenient, if not quite correct.

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*weights* on the new scale are the same as the combining weights; and therefore with *any* standard they are *proportional to the combining weights*. This suggests a uniform method for choosing the combining weights of compounds. Let them be *always* so chosen as to be proportional to the specific weights of the substances in the gaseous state. This convention has been adopted. It only remains to select a standard combining weight to which to refer all others. Hydrochloric acid has been chosen, because hydrogen forms only this compound with chlorine (1 part of hydrogen to 35.5 of chlorine); so that if 1 be taken as the combining weight of hydrogen, that of chlorine is 35.5, without any alternative, so far as it is referred to hydrogen. The combining weight of hydrochloric acid is thus 36.5. As specific weights of gases and vapours are generally referred to air as unity, it will be convenient to derive an equation for calculating the combining weight ( $C'$ ) of any compound gas or vapour from its specific weight (*gas density*)  $S'$ . According to the convention—

$$C : C' :: S : S';$$

and for hydrochloric acid gas  $C = 36.5$ , and  $S = 1.265$ . Substituting these values—

$$36.5 : C' :: 1.265 : S'$$

and 
$$C' = S' \times \frac{36.5}{1.265} = S' \times 28.87.$$

When the specific weights are referred to hydrogen as unit, a very simple relation appears between specific weights and combining weights. The specific weight of air referred to hydrogen as standard is 14.435 nearly. Dividing the former value for  $C'$  by this number,

its value referred to hydrogen as standard is obtained :—

$$C' = S' \times \frac{28.87}{14.435} = 2S'.$$

That is, *the combining weight of a gaseous compound is twice its specific weight referred to hydrogen as standard.* Combining weights determined in this way are only approximate, being affected by errors due to the difficulty of obtaining accurately the weight and volume of a gas or vapour. As will be seen immediately, they can be corrected by adding together the combining weights of the elements in the compound, these combining weights having all the accuracy which can be attained by exact weighings of liquids and solids in analytical operations.

A few examples will make clear the manner in which the *method of gas density* is applied to the selection of combining numbers for the elements. A vast amount of labour has been expended in determining accurately the composition of water. For 1 part by weight of hydrogen water has 7.98 parts of oxygen. It remains to discover what multiple of the latter number is to be taken as the combining weight of oxygen. In the following table there are given, neglecting small fractions, the specific weights (air = 1) (I.), combining weights (II.), percentage of oxygen (III.), and the quantities of oxygen in the combining weights (IV.), of a number of gaseous or gasifiable oxygen compounds. The numbers in the last column are calculated as follows :—

Specific weight of gaseous water, 0.623, multiplied by 28.87 gives its combining weight—

$$0.623 \times 28.87 = 17.98601, \text{ say } 18.$$

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Analysis of water shows that 88·89% of this (or 15·98, say 16) is oxygen :—

COMPOUNDS.	I.	II.	III.	IV.
Water .....	0·623	18	88·89%	16
Carbon monoxide .....	0·967	28	57·14%	16
Carbon dioxide .....	1·524	44	72·72%	32
Nitrogen monoxide .....	1·527	44	37%	16
Nitrogen dioxide .....	1·041	30	53·3%	16
Nitrogen tetroxide .....	1·58	46	71%	32
Sulphur dioxide .....	2·23	64	50%	32
Sulphur trioxide .....	2·77	80	60%	48

The smallest quantity of oxygen found in the combining weight of any of the oxygen compounds is thus seen to be 16. In all the large number of oxygen compounds submitted to this test no smaller quantity has been found. Therefore, 16 is the approximate combining weight of oxygen. The accurate combining weight is  $7·98 \times 2 = 15·96$ .

The numbers determined by the method of gas density and corrected by a reference to the composition of compounds as determined by analysis, depend for their accuracy on the analytical methods employed. The greatest perfection in these has been reached by J. S. Stas, and the following example of his work is added (without explanation) to show the degree of accuracy attained. This is marked by the close agreement of the numbers in the third column :—

POTASSIUM CHLORIDE TAKEN.	SILVER TO DECOMPOSE IT.	COMBINING WEIGHT OF SILVER.
7·450g	10·7807	107·9399
7·450g	10·7810	107·9404
7·450g	10·78094	107·9398
7·450g	10·7809	107·9394
7·450g	10·7811	107·9386
2·0945g	3·03086	107·9361
22·3500g	32·3428	107·9398

4. **The Law of Specific Heat.**—The method of gas density has been applied particularly to the non-metals, as they generally form many gasifiable compounds. Many of the metals have not so far yielded compounds gasifiable at temperatures which permit a determination of gas density. But another method of determining combining weights is at hand which can be used with particular facility in the case of metals. The following table indicates the nature of this law :—

ELEMENT.	COMBINING WT. (by gas density).	SPECIFIC HEAT.	COMBINING WT. × SPECIFIC HEAT.
Phosphorus .....	31	0.2020	6.2
Zinc .....	65	0.0956	6.3
Arsenic .....	75	0.0830	6.3
Tin .....	118	0.0560	6.5
Antimony .....	120	0.0508	6.1
Mercury .....	200	0.0319	6.4
Lead .....	207	0.0314	6.5

The specific heats are for the *solid* elements. A glance at this table shows that the larger the combining weight the smaller the specific heat of the elements ; and, further, the product of the combining weight and the specific heat is approximately the same for all the elements included in this table. The same has been found to hold true for nearly all the elements the specific heats of which have been determined for the solid state, and the combining weights of which have been found by the method of gas density. The exceptions are beryllium, boron, carbon, and silicon, the specific heat of which increases rapidly with rise of temperature ; so that the product of specific heat and combining weight which is much less than 6.3 at low temperatures approximates to that number at high temperatures. It may be assumed then that

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we have here a general law applicable to all the elements. *The product of the combining weight and the specific heat of an element is 6.3 (approximately).* If the specific heat of an element is known, its combining weight can, then, be found (approximately) by dividing 6.3 by its specific heat. The metals of the alkalis and alkaline earths do not yield easily gasifiable compounds; but they have been obtained pure and their specific heats determined; and their combining weights have been settled upon by the method just indicated. Analysis of magnesium sulphate has shown that the *equivalent weight* of magnesium, *i.e.* the weight of magnesium combined with eight parts of oxygen, is 12.19. Its specific heat is 0.245. Its approximate combining weight is therefore  $\frac{6.3}{0.245} = 25.6$ . From this it is plain that its accurate combining weight is  $12.19 \times 2 = 24.38$ . Again, the analyses of Stas (see p. 11) have fixed the equivalent of silver as 107.94. Its specific heat is 0.056. Its approximate combining weight is therefore  $\frac{6.3}{0.056} = 112$ ; which is near enough to 107.94 to justify us in choosing this number as the accurate combining weight.

It has been found, too, that the specific heats of solid compounds multiplied by their combining weights usually give numbers which are approximately multiples of 6.3\*. For example, the specific heat of lead sulphide ( $\text{PbS}$ ) is 0.053. Its combining weight (reckoned as equal to that of lead added to that of sulphur) is 239. The product of these is about  $12.6 = 2 \times 6.3$ . Again, for red lead ( $\text{Pb}_3\text{O}_4$ ), the numbers are 0.0616 and 621 (*i.e.*  $3 \times 207 + 4 \times 16$ ).

$$621 \times 0.0616 = 42.196 = 7 \times 6.0 \text{ nearly.}$$

\*The approximation is not very close for many compounds of gaseous elements like oxygen and hydrogen.

From these examples it seems that the elements carry with them into their compounds their capacity for heat. It can also be deduced that the specific heat of *solid* oxygen is such that when multiplied by its combining weight the product is not far removed from 6. But in the case of many solid oxygen compounds the number must be considerably less. To solid compounds of those elements which in the free state come under the *law of specific heat*, the following law applies: *The product of the specific heat of a solid compound and its combining weight is approximately equal to  $n \times 6.3$ ,  $n$  indicating the number of times the combining weights of the elements are taken to make the combining weight of the compound.*

**5. The Law of Isomorphism.**—*Crystals* are the more or less regular geometrical forms assumed by most substances when they pass from the liquid or gaseous to the solid state. Every crystal when carefully studied is seen to be bounded by surfaces which are arranged with more or less symmetry around certain (imaginary) *axial lines*. In actual crystals, however, it is more a *symmetry of direction* than of position, as the conditions of growth usually prevent equally rapid growth on the different faces. Thus one face becomes further removed from the centre of the figure than another, and *distortion* results. By imagining all the like surfaces of any crystal to be equally developed, one gets an *ideal form*, in which the surfaces running in similar directions with regard to the axes of reference are all of the same size and shape. *Simple forms* are bounded by like surfaces; two or more simple forms may be combined in the same crystal. In general, there are certain planes which can divide a crystal form into two halves such that one is the mirror image of the other.

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These planes are *planes of symmetry*; and forms differ in the number of their planes of symmetry. A central line perpendicular to a plane of symmetry is an *axis of symmetry*.

It has been found that all crystal forms can be grouped in **SIX SYSTEMS**, defined by their axes of reference and their planes of symmetry. They are as follows:—

(1) **THE CUBIC SYSTEM.**—Three axes, equal and at right angles to each other. Nine planes of symmetry.

(2) **THE TETRAGONAL SYSTEM.**—Three axes at right angles to each other, two of them being equal and the third longer or shorter. Five planes of symmetry.

(3) **THE HEXAGONAL SYSTEM.**—Four axes; three being equal, in the same plane, and at angles of  $60^\circ$  to each other, the fourth being longer or shorter than the three and at right angles to their plane. Seven planes of symmetry.

(4) **THE RHOMBIC SYSTEM.**—Three unequal axes at right angles to each other. Three planes of symmetry.

(5) **THE MONOCLINIC SYSTEM.**—Three unequal axes, two being inclined to each other and the third at right angles to their plane. One plane of symmetry.

(6) **THE TRICLINIC SYSTEM.**—Three unequal and inclined axes. No plane of symmetry.

The crystal forms of substances are valuable aids to their recognition. Except in the cubic system where the axes are all equal, the *axial ratios* are different for all substances crystallising in forms of the same system.

There are, however, exceptions to this rule. There are groups of similar substances which crystallise in the same forms, and which are so like in their properties that a crystal of one will grow in a saturated solution of another of the group, preserving the same form. Such substances are said to be *isomorphous* (Greek *isos*, equal, and *morphē*, form). It is found that *the chemical formulas of isomorphous substances are similar*. Thus, the isomorphous sulphates crystallising with water :—

Green vitriol.....	.....	$\text{Fe SO}_4 \cdot 7\text{H}_2\text{O}$
White vitriol.....	.....	$\text{Zn SO}_4 \cdot 7\text{H}_2\text{O}$
Cobalt sulphate .....	.....	$\text{Co SO}_4 \cdot 7\text{H}_2\text{O}$
Nickel sulphate .....	.....	$\text{Ni SO}_4 \cdot 7\text{H}_2\text{O}$

These formulas differ only in the symbols for the metals, and in each formula the symbol for the metal is single. The resemblance would be imperfect if that for green vitriol were  $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  (Fe being 28 instead of 56). It is reasonable to suppose that, if another sulphate is found isomorphous with these, the combining weights should be so chosen as to give a formula similar to those of green vitriol, white vitriol, etc. *Manganous sulphate* is isomorphous with green vitriol. By analysis of the sulphate, the equivalent weight of manganese has been found to be 27·51. If this be taken as the combining weight, the formula for the sulphate will be  $\text{Mn}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ . As this would be different from that of the other members of this isomorphous group, it is reasonable to take  $2 \times 27\cdot51$  as the combining weight, when the formula becomes  $\text{Mn SO}_4 \cdot 7\text{H}_2\text{O}$ , symmetrical with the others. The elements which play the same part in isomorphous compounds are commonly spoken of as *isomorphous elements*.

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The Law of Isomorphism is as follows :—*Isomorphous elements replace each other in isomorphous compounds in the proportion of the combining weights of the elements*

The following are the common groups of isomorphous elements :—

- I.—Fluorine, chlorine, bromine, iodine; manganese (perchlorates and permanganates are isomorphous).
- II.—Lithium, sodium potassium, rubidium, caesium, [ammonium]; silver and thallium form *alums* in which they take the place of potassium in common alum.
- III.—Calcium, strontium, barium, lead (in sulphates, phosphates, etc.); iron, zinc, magnesium, manganese (in carbonates, sulphates, etc.); nickel, cobalt, copper (in sulphates).
- IV.—Sulphur, selenium, tellurium, chromium.
- V.—Arsenic, antimony, bismuth, vanadium, nitrogen, phosphorus.
- VI.—Aluminum, iron, chromium, manganese (in alums).
- VII.—Platinum, iridium, palladium, rhodium, ruthenium, osmium.
- VIII.—Carbon, silicon, titanium, zirconium, thorium, tin.
- IX.—Copper, silver, gold (in their chlorides, sulphides, and double cyanides).

The law of isomorphism has been of assistance in deciding doubtful cases, where the methods of gas density and of specific heats have either been difficult of application or have yielded conflicting results. In such cases, those multiples of the equivalent weights have been taken which give similar formulas for isomorphous compounds of the elements.

6. **The Periodic Law** (Newlands, 1864; Mendeléeff, 1869; L. Meyer, 1870).—From the preceding sections it can be seen that the properties of the elements are closely connected with those numbers which express the proportions in which they enter into combination; and the farther investigation is carried, the closer is this connection found to be. The relation between the combining weights and the other properties of the elements has its most general expression in the *Periodic Law*. When the elements are arranged in the order of their combining weights beginning with *lithium* (hydrogen is omitted because it does not fall naturally into any group of elements) and following with beryllium, boron, carbon, nitrogen, oxygen, and fluorine, the 8th element, *sodium*, is like the 1st, the 9th like the second, and so on to the 15th, *potassium*, which is again like the 1st. This suggests the idea that *all* the elements may in the same way be found to fall into families or groups of like elements when arranged in this way. The following table shows this to be the case, allowance being made for undiscovered elements, and for certain deviations from the simple series of seven elements, after the first two series are completed :—

## CLASSIFICATION OF THE ELEMENTS ACCORDING TO THE PERIODIC LAW.

## GROUPS.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H = 1							
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 58.5 Ni = 59
5	Cu = 63.5	Zn = 65	Ga = 70	Ge = 72	As = 75	Se = 79	Br = 80	Ru = 101 Rh = 104 Pd = 106
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 97		
7	Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 125	I = 127	
8	Cs = 133	Ba = 137	La = 138	Ce = 140				
9								
10			Yb = 173		Th = 182	W = 184		Os = 194 Ir = 193 Pt = 196
11	Au = 198	Hg = 200	Tl = 204	Pb = 206	Bi = 208			
12				Th = 232		V = 240		

SERIES.

The relations to each other of the elements as arranged in the table can be studied in two ways, 1st in horizontal series, as Li, Be, B, C, N, O, F; and 2nd in vertical groups, as Li, Na, K, Cs, Rb, Ag, Cu, Au. As the third series is made up of commoner elements, it will serve as a good example for study; *Sodium* is well known as an *alkali metal*, characterised by decomposing water at ordinary temperatures and forming a freely soluble hydroxide ( $\text{NaOH}$ ) of strongly *basic* properties. It is a true *metal*, with the characteristic metallic lustre. Its oxides show no tendency towards acidic character.—*Magnesium* is also a well-marked metal; but it does not decompose water at ordinary temperatures, and only slowly at  $100^\circ$ . Its hydroxide,  $\text{Mg}(\text{OH})_2$ , is practically insoluble in water (1 part in 55,000). It is a moderately strong base, but many of its salts are decomposed in whole or in part when their aqueous solutions are evaporated to dryness. Thus:—



Sodium chloride ( $\text{NaCl}$ ) is not decomposed by water. In fact magnesium is decidedly less powerful in its basic character than sodium, but it shows no acidic properties.—*Aluminum* is a metal in lustre and other properties. It does not, however, decompose water at any temperature. Its only hydroxide,  $\text{Al}(\text{OH})_3$ , is insoluble in water. The hydroxide forms soluble compounds both with strong acids and with strong bases; but it does not combine with weak acids or weak bases. Aluminum has therefore a dual character, possessing both basic and acid properties, but neither in a very marked degree. This dual character is manifested in an ordinary test for aluminum in salt solutions. If to a solution of aluminum

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chloride ( $\text{AlCl}_3$ ), solution of sodium hydroxide is added, a gelatinous precipitate of aluminum hydroxide is thrown down :—



Here the inferior basic character of aluminum hydroxide is shown. When a further quantity of sodium hydroxide is added, the precipitate redissolves and the solution is then found to contain *sodium aluminate*, a salt in which aluminum is the acidic element.—*Silicon* is well known in its acidic oxide *silica*,  $\text{SiO}_2$ . The element itself is not metallic in appearance. Silicic acid is a weak acid. In passing from aluminum to silicon we have left behind the basic character, but have not yet reached an element of more than weakly acidic properties. The next element in the series, *phosphorus*, has the characters of a decidedly acidic element. This is shown in its acids, hypophosphorous, phosphorous, and phosphoric, the latter being well marked in its acid properties.—*Sulphur*, the sixth member of the series, shows the acidic character even more strongly than phosphorus. In combination with oxygen and hydrogen it forms numerous acids, one of which, sulphuric acid, is in many respects the most powerful of acids. None of the oxides of silicon, phosphorus, or sulphur show any tendency to enter into saline combination with true acids. Sulphur even forms a feeble acid by combining with hydrogen alone. Hydrogen sulphide,  $\text{H}_2\text{S}$ , reddens blue litmus. The hydrogen compounds of silicon and phosphorus have no acid properties; and sulphur may be considered to show in this respect its greater power as an acid-forming element.—In *chlorine*, the last member of the series, this power is found at its maximum. Chlorine not only forms several

acids ( $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ ), with hydrogen and oxygen, but it combines with hydrogen alone to form a powerful acid, viz: hydrochloric acid ( $\text{HCl}$ ).—This series begins with sodium, an element of strongly basic character, and, passing through elements of decreasing basic and of increasing acidic characters, ends with chlorine, a powerful acid-forming element. In the 2nd series the same progression from basic to acidic character can be traced; and, indeed, with certain modifications, in all the series. The modifications can be seen in the 4th and 5th series. The 4th series begins with *potassium*, a metal of the alkali family. The seventh element from this is *manganese*, a basic element, as seen in the manganous salts,  $\text{MnSO}_4$ ,  $\text{MnCO}_3$ ,  $\text{MnCl}_2$ , etc., but also acidic in the *manganates* and *permanganates*. Then follows a trio of very similar elements, *iron*, *cobalt*, and *nickel*, which, having no likeness to sodium or potassium, are put in an additional group—VIII. The next element, *copper*, has a few points of likeness to the alkali metals and begins the 5th series, but no strongly acidic element is reached before *arsenic*, *selenium*, and *bromine*, at the end of this series; and at the beginning of the 6th we find *rubidium*, an alkali metal. The 6th and 7th series show the same features as the 4th and 5th; and, so far as the fragmentary character of the remaining series allows us to judge, they, too, fall into pairs. Thus, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine constitute the first *period*, i.e. the elements from the first. lithium, to the next of the same kind, sodium. (The *periodic* recurrence of like elements in this scheme has given to the law here revealed its name, *the periodic law of the elements*.) The 2nd period also consists of seven elements, viz.: those of the third series. But the 3rd includes two

series, for iron, cobalt, and nickel, beginning the next alkali series. The 3rd series is not found, always su- same group of their co- four long fragment passing al- the acidic regular m- of the *th* Where ne-

$\text{R}_2\text{O}$	$\text{R}_2\text{O}$
$\text{Li}_2\text{O}$	$\text{Be}$
$\text{Na}_2\text{O}$	$\text{Mg}$
$\text{K}_2\text{O}$	$\text{Ca}$
$\text{Cu}_2\text{O}^\dagger$	$\text{Zn}$
$\text{Rb}_2\text{O}$	$\text{Sr}$
$\text{Ag}_2\text{O}$	$\text{Cd}$
$\text{Cs}_2\text{O}$	$\text{Ba}$
$\text{Au}_2\text{O}$	$\text{Hg}$

NOTE.—R is

\*The elements because they form another.

†Copper has

‡A higher ac-

series, for the 8th element from potassium is (omitting iron, cobalt, and nickel) copper, and it is only at the beginning of the 6th series that we find rubidium, the next alkali metal. Similarly for any element after the 3rd series; another element with strong likeness to it is not found until the 15th is reached, although the 8th is always sufficiently like it to justify its being placed in the same group. Thus the elements arranged in the order of their combining weights form two *short periods* and four *long periods*, with thorium and uranium as a fragment of a seventh\*.—The gradation in properties in passing along the series appears in properties other than the acidic and basic. The *types* of compounds vary in a regular manner. In the following table are the formulas of the *highest* basic or acid oxide of each element. Where necessary for uniformity the formulas are doubled.

$R_2O$	$R_2O_2$	$R_2O_3$	$R_2O_4$	$R_2O_5$	$R_2O_6$	$R_2O_7$	$R_2O_8$
$Li_2O$	$Be_2O_2$	$B_2O_3$	$C_2O_4$	$N_2O_5$			
$Na_2O$	$Mg_2O_2$	$Al_2O_3$	$Si_2O_4$	$P_2O_5$	$S_2O_6$	$[Cl_2O_7]$	
$K_2O$	$Ca_2O_2$	$Sc_2O_3$	$Ti_2O_4$	$V_2O_5$	$Cr_2O_6$	$Mn_2O_7$	
• $Cu_2O^\dagger$	$Zn_2O_2$	$Ga_2O_3$	$Ge_2O_4$	$As_2O_5$	$Se_2O_6$		
$Rh_2O$	$Sr_2O_2$	$Y_2O_3$	$Ti_2O_4$	$Nb_2O_5$	$Mo_2O_6$	$[I_2O_7]$	
$Ag_2O$	$Cd_2O_2$	$In_2O_3$	$Zr_2O_4$	$Sb_2O_5$	$Te_2O_6$		
$Cs_2O$	$Ba_2O_2$	$La_2O_3$	$Ce_2O_4$	$Ta_2O_5^\ddagger$	$W_2O_6$	.....	$Os_2O_8$
$Au_2O$	$Hg_2O_2$	$Yb_2O_3$	$Pb_2O_4$	$Bi_2O_5$	$U_2O_6$		
.....	.....	$Tl_2O_3$	$Th_2O_4$				

NOTE.— $R$  is a general symbol to indicate the *type* of compound.

\*The elements of group VIII. are commonly spoken of as *transition elements*, because they form a link between the end of one series and the beginning of another.

†Copper has a higher basic oxide,  $CuO$ .

‡A higher acid oxide  $UO_4$  is known.

In all these formulas the symbols of the elements combined with oxygen are taken the same number of times. In each case twice the combining weight is represented. The number of oxygen combining weights may then be considered to represent the relative *combining capacities* or values of the elements for oxygen (that of hydrogen, lithium, etc., being taken as one); and this is seen to increase from one to eight. The seventh and eighth columns are almost blank, but the blanks may be filled to some extent by compounds other than the oxides. Chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , is not known, but the corresponding acid, perchloric acid,  $\text{HClO}_4$ , may be taken to indicate that chlorine has a combining capacity (value) of seven. Similarly for iodine. The recent discovery of *nickel carbonyl*,  $\text{Ni}(\text{CO})_4$ , shows nickel to have a maximum combining capacity of eight. For the combining capacity of carbonyl is two, as shown by its combination with oxygen in carbon dioxide,  $\text{CO}_2$ \*. In their combining capacities for hydrogen the elements are somewhat different, but they show in this case also that their properties are of a periodic character. As comparatively few of the elements form distinct compounds with hydrogen, the demonstration cannot be made so complete as with the oxides. Compounds of the metals of the first three groups with univalent radicles are inserted in the table, where hydrogen compounds are not known. The radicle  $\text{CH}_3$  is equivalent to one part of hydrogen, as can be seen in the formula  $\text{CH}_3\text{Cl}$ .

\* The combining capacity of oxygen is two, as shown by the formula for water,  $\text{H}_2\text{O}$ .

RH

 $\text{Li}(\text{CH}_3)$  $\text{Na}(\text{CH}_3)$ 

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RH	RH <sub>2</sub>	RH <sub>3</sub>	RH <sub>4</sub>	RH <sub>5</sub>	RH <sub>6</sub>	RH
Li(CH <sub>3</sub> ) <sub>3</sub>	Be(CH <sub>3</sub> ) <sub>2</sub>	BH <sub>3</sub>	CH <sub>4</sub>	NH <sub>3</sub>	OH <sub>2</sub>	FH
Na(CH <sub>3</sub> ) <sub>3</sub>	.....	Al(CH <sub>3</sub> ) <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	SH <sub>2</sub>	CH

The maximum combining capacity for hydrogen (four) is reached in the middle of the series, from which there is a decrease to one. The point to be noted in these tables is that *each series* shows with more or less completeness the *same* regular variation in the combining capacity of its elements. Similar tables can be made for the hydroxides, chlorides, bromides, iodides, etc.

The periodic recurrence of like properties is found, too, in those physical properties which can be exactly measured and expressed mathematically. Such are specific weight, conductivity for heat and electricity, melting point, boiling point, etc. If the combining weights of the elements be divided by their specific weights for the solid state, the numbers obtained are the relative volumes of the combining weights of the elements. They are the *combining volumes* of the *solid* elements. Most of the elements have been obtained in the solid state, so that the table of combining volumes is pretty complete. The relation of the combining weights to the combining volumes of the (solid) elements can best be shown by measuring off from two lines meeting at right angles distances proportional to the combining weight and combining volume of each element, and connecting the points thus obtained by a continuous line. Thus is obtained the *curve* of combining weights and combining volumes. This is called a *periodic curve*, consisting, as it does, of a series of waves.



*Like elements occupy like positions* on the ascending and descending parts of the curves. Thus, the alkali metals occupy the summits, the other metals are generally found along the descending parts, and the non-metals along the ascending parts of the curve. Of the waves, the first two are short, corresponding to the short periods; the rest are long, corresponding to the long periods. *The periodic recurrence of like elements* is thus graphically demonstrated.

As a consequence of the double length of the periods after the first two, the corresponding elements of the two series constituting a long period do not have the same likeness to each other which is found between corresponding elements in the short periods. Thus each group subdivides after the first two elements into two families. In group I., potassium, rubidium, and caesium form one family; and copper, silver, and gold, the other. The distinction between the families is more or less marked in the different groups. In groups I. and VII. the family are stronger than the group resemblances; for, certainly, copper, silver and gold are more like each other both physically and chemically than they are like any of the alkali metals. Also, there are few resemblances between manganese and the halogen family. In groups II., III., V., and VI. the group and family resemblances are pretty evenly balanced; while in IV. the group characteristics prevail.

No general statement can be made with regard to the first two elements of each group. In group I. they evidently both belong to the alkali family. So, fluorine and chlorine of group VII. both belong to the halogen family.

In the other groups they seem to combine more or less the characteristics of both families.

The first group will serve to illustrate the nature of the classification. It includes the metals of the alkalis, lithium, sodium, potassium, rubidium, and caesium, together with the three heavy metals, copper, silver, and gold. Between the two families the resemblance is not very strong, so that the *group characteristics* are reduced to a general resemblance in the type of compounds, e.g.,  $MCl$ ,  $M_2O$ , etc., where  $M$  stands for any metal of the group. However, silver forms an alum in which it plays the part of an alkali metal. The *family characteristics* on the other hand are well defined. Those of the alkali family are given at p. 368 of the Text Book. To the statement given there may be added the formation of isomorphous alums (p. 336 of Text Book), of other double sulphates, and of chloroplatinates (p. 314). These series of compounds show the *gradation in properties* generally well marked in the natural families of the elements. This is well shown in the solubilities of the alums and chloroplatinates, which decrease from lithium to caesium. The same feature is seen in the physical properties of the metals:

	COMBINING WEIGHT.	MELTING POINT.	BOILING POINT.	SPECIFIC WEIGHT*.	FLAME COLOUR.
Lithium.....	7	180°	Above 1000°	0.59	Red
Sodium....	23	95°	Above 900°	0.98	Yellow
Potassium..	39	58°	720°	0.87	Violet
Rubidium..	85	39°	.....	1.52	Violet
Cæsium....	133	27°	.....	1.88	Blue

\* See p. 25.

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Copper, silver, and gold are not so closely related to each other as are the metals of the alkalis. Still they have many points of resemblance. They are heavy, durable metals difficult to oxidise, and therefore valuable in the arts and manufactures. Each of them forms a white chloride of the type  $MCl$  ( $CuCl$ ,  $AgCl$ ,  $AuCl$ ), insoluble in water but soluble in ammonia solution. They also form basic oxides of the same type, viz.:  $Cu_2O$ ,  $Ag_2O$ , and  $Au_2O$ . But copper forms compounds of another type,  $CuO$ , etc. These cupric compounds are in some cases isomorphous with the corresponding compounds of iron and zinc. Thus copper forms a connecting link between the first and second series of this long period. Gold forms an acid oxide,  $Au_2O_3$ . *Auric acid*,  $HAuO_2$ , is a weak acid, but forms crystallisable salts of the alkali metals. These with *chlorauric acid*,  $HAuCl_4$ , and its salts recall similar compounds of boron and aluminum. These compounds of copper and gold are examples of many similar cases in which elements of one group have a distinct resemblance to those of another. In fact, it follows from the gradation in properties both in the series and in the groups, that each element must bear a resemblance more or less close to the four elements next it in the family and the series to which it belongs. But apart from this there are apparently irregular likenesses, as that of thallium to the alkali metals, of chromium to aluminum, and of titanium to iron. Indeed, the periodic law places manganese in the same group with the halogens with which it has very few affinities, and separates it from iron, nickel, and cobalt which it resembles much more; so that for practical purposes (for chemical analysis, etc.) this classification needs to be considerably modi-

fied. But a careful study of the whole system will show that to a large extent the properties in common which justify the natural classification of the elements are the properties upon which the analyst depends for the practical separation of the elements into groups and families.

The use of the periodic law in settling doubts with regard to the choice of combining weights is obvious. The equivalent weight of beryllium was found to be 4.5. In its chemical properties it was found to resemble boron and aluminum, its oxide would thus have the formula  $\text{Be}_2\text{O}_3$  with  $\text{Be} = 3 \times 4.5$ . But the element showed closer relationship to magnesium. In order to be classed with this element its oxide must be  $\text{BeO}$  (like  $\text{MgO}$ ) with  $\text{Be} = 2 \times 4.5$ . A determination of the specific heat of the element (0.42) favoured the first value; for  $\frac{0.3}{0.42} = 15$ . The classification by the periodic law settles the difficulty. An element with combining weight 13.5 would come between carbon and nitrogen where there is no place for it. With the combining weight 9 it comes between lithium and boron, and here there is a vacant place for it. The periodic law has also been used in predicting the properties of undiscovered elements and their compounds. Gallium, scandium and germanium have been discovered since Mendeléeff published his *Periodic Law of the Elements* with its accompanying description of the properties of elements which would fit in between calcium and titanium, and between zinc and arsenic. The following parallel description (from Richter's *Inorganic Chemistry*) shows the remarkable agreement in the case of germanium between the predicted \* and the discovered elements:—

\* Called *eka-silicon* by Mendeléeff.

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† See p. 25.

## EKA-SILICON, ES.

Combining wt. about 72.  
 Density, 5.5.  
 Combining vol.,† 13 nearly.  
 Form of oxide,  $\text{EsO}_2$ .  
 Sp. gr., 4.7.  
 Easily obtained by reduction with carbon or sodium.  
 Dirty gray metal, fuses with difficulty, forming the oxide when heated in the air.  
 Will form a chloride,  $\text{EsCl}_4$ , which will boil near  $100^\circ$ , probably lower.  
 Its sulphide will be insoluble in water, but probably soluble in ammonium sulphide.  
 Will be scarcely acted on by acids.

## GERMANIUM, GE\*.

Combining wt. 72.32 and 72.28.  
 Density, 5.69.  
 Combining vol., 13.25.  
 Forms an oxide,  $\text{GeO}_2$ .  
 Sp. gr., 4.703.  
 Easily obtained by reduction with carbon or hydrogen.  
 A gray-white metal, fusing at  $900^\circ\text{C}$ . and forming the oxide when heated in air.  
 Forms the chloride,  $\text{GeCl}_4$ , boiling at  $86^\circ\text{C}$ .  
 The sulphide is moderately soluble in water, more readily in ammonium sulphide.  
 Not acted on by acids.

**7. Reversal of Chemical Changes.**—Chemical change is influenced by various conditions, such as temperature, pressure, etc.; and changes which go on under certain conditions may be *reversed* when the conditions are changed. Such reversals of chemical change are quite commonly brought about by change of *temperature*. If mercury be heated to near its boiling point in air or oxygen it slowly combines with oxygen and forms the red oxide. If now the temperature be raised, the oxide is decomposed again into its elements. When barium monoxide ( $\text{BaO}$ ) is heated to about  $300^\circ$  in a current of air, it combines with the oxygen of the

\* Discovered in 1886 by Dr. Clemens Winkler of Freiberg.

† See p. 25.

air and forms the dioxide ( $\text{BaO}_2$ ). But, when the temperature is raised, this change is reversed, the dioxide breaking up into the monoxide and oxygen. Advantage has been taken of this reversal in Brin's method of manufacturing oxygen from the air. Equations representing such reversible actions are, like algebraic equations, true when read either way, as :—



*Dissociation* by heat into gaseous products which recombine when the temperature is lowered comes under the head of reversible changes. The decomposition of barium dioxide may be regarded as dissociation, since the oxygen recombines when the temperature is lowered. But a typical example of dissociation is seen in the case of *ammonium chloride*, the gas density of which was found to be only half that calculated from the formula  $\text{NH}_4\text{Cl}$ ; that is, a given weight occupied twice the calculated volume. This suggested the idea that the double volume is due to the decomposition of the ammonium chloride into two gases. This can be proved to be the case by a simple experiment. Heat a little ammonium chloride in a covered platinum crucible until it is volatilised. Remove the cover and insert quickly a strip of moistened blue litmus paper. It is turned red. The ammonium chloride was dissociated into ammonia and hydrochloric acid. The former, being the lighter gas, diffused out more rapidly, so that the remainder was acid in reaction. By a more complicated apparatus the separation by diffusion can be effected in such a way as to show the presence of each of the gases. *Phosphorus pentachloride*,  $\text{PCl}_5$ , is an example of a volatile substance which dissociates

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\* See p. 9.

† Phosphor  
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partly into the trichloride and chlorine when volatilised, but more and more as the temperature is raised. Its theoretical specific weight referred to air is  $\frac{208.5}{29.927} = 7.26$ .\* The specific weights at different temperatures as found by experiment are given in the following table :—

TEMPERATURE.	SPECIFIC WT.
182° .....	5.078
190° .....	4.987
200° .....	4.851
230° .....	4.302
250° .....	3.991
276° .....	3.84
288° .....	3.67
289° .....	3.69
300° .....	3.65

The specific weight of a mixture of equal volumes† of phosphorus trichloride and chlorine is 3.61; from which it may be concluded that the dissociation of phosphorus pentachloride is almost complete at 288°. In this case the dissociation is evident to the eye, as it is accompanied by the appearance of the greenish yellow colour of free chlorine. As the temperature rises the colour becomes stronger, and as it falls it becomes weaker again owing to reversal of the chemical change.

Chemical changes may also be *limited* and reversed by conditions of gaseous *pressure*. This is seen in the decomposition of calcium carbonate by heat. If calcium carbonate be heated to 930° in a vacuum, decomposition goes on until the carbon dioxide exerts a pressure equal to about 520mm. of mercury. Then the decomposition

\* See p. 9.

† Phosphorus trichloride and chlorine combine in equal volumes to form the pentachloride.

ceases unless the pressure of the carbon dioxide is lowered. On the other hand if the pressure is increased, recombination takes place until the pressure is again equal to 520mm. In "burning" limestone it is necessary to remove the carbon dioxide as it is set free, otherwise the decomposition would cease as soon as the pressure of the gas reached a certain limit. This removal is effected by the free draught of hot gases through the kiln.

Another important condition influencing chemical change is the relative quantities of substances present, *i.e.* the *action of mass*. When a solution of bismuth trichloride in water is diluted with water, a white precipitate appears, which increases with the quantity of water added. It is an oxychloride of bismuth formed by the action of the water:—



If enough hydrochloric acid be added the precipitate is redissolved; *i.e.*, the change represented by the equation is reversed. The addition of more water causes the precipitate to reappear, and so on. Here, then, is a case in which the direction which a chemical change is to take is determined by the relative masses of the reacting substances. If in a solution of bismuth trichloride the proportion of water to that of hydrochloric acid exceeds a certain limit, the water is able to decompose some of the bismuth trichloride; but, by then increasing the proportion of hydrochloric acid the action is reversed and the trichloride is formed again. Another good example of mass-action is seen in the oxidation of iron by heating it in a current of steam. When iron is heated to redness in an atmosphere of steam the iron is oxidised

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and hydrogen is set free. But, if an oxide of iron is heated in an atmosphere of hydrogen, iron is reduced and water is formed. This goes on until the atmosphere contains certain proportions of hydrogen and water, and then no further reduction takes place. The same limit is reached when iron is heated in an atmosphere of water vapour. It is therefore possible to make a mixture of hydrogen and water vapour which will neither oxidise iron nor reduce oxides of iron. If in such a mixture the proportion of water vapour is increased, the mixture becomes capable of oxidising iron at a red heat; but if the proportion of hydrogen is increased, the reverse action, viz., the reduction of iron oxides, is brought about.

The influence of mass on chemical change is much more extensive than was at one time thought. Chemical changes can be brought about which were formerly thought to be impossible. Chlorine easily displaces bromine from its compounds with metals, and at first sight it would seem impossible to reverse this substitution; but if sodium chloride be heated in a closed tube with bromine, a certain proportion of the chlorine is displaced by the bromine, and *this proportion is increased by increasing the quantity of bromine in the tube*. Here the action of mass is very plain.

**8. Raoult's Law.**—It is a well-known fact that salt water requires a lower temperature to freeze it than pure water does. The freezing point of solvents is in general lowered by the presence in them of dissolved substances; and the amount by which the freezing point is lowered is, for the same substance, approximately proportional to the percentage of the dissolved substance\*. Thus the freez-

\* This applies only to dilute solutions.

ing points of aqueous solutions of sodium chloride containing 1, 5, and 10 grams of the salt to 100 of water are respectively  $-0^{\circ}58$ ,  $-2^{\circ}91$ , and  $-6^{\circ}10$ ,—numbers nearly proportional to 1, 5, and 10. When the effects of different compounds are compared, a remarkable law appears. For very dilute solutions, *the freezing point of any solvent is lowered to the same extent by weights of the dissolved compounds proportional to the combining weights.* The following table\* shows the approximation to exactness of this law when water is the solvent used. Ice begins to form in aqueous solutions at the temperatures given in column III, when 1000 grams of water contain the combining weight (in grams) of the dissolved substances (column II.)

I. DISSOLVED SUBSTANCES.	II. TO 1000 GRAMS OF WATER.	III. FREEZING POINT.
Methyl Alcohol, $\text{CH}_3\text{O}$ .....	32	$-1^{\circ}73'$
Glycerine, $\text{C}_3\text{H}_5\text{O}_3$ .....	92	$-1^{\circ}71'$
Sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .....	342	$-1^{\circ}85'$
Phenol, $\text{C}_6\text{H}_5\text{O}$ .....	94	$-1^{\circ}55'$
Acetic Acid, $\text{C}_2\text{H}_4\text{O}_2$ .....	61	$-1^{\circ}90'$
Oxalic Acid, $\text{C}_2\text{H}_2\text{O}_4$ .....	90	$-2^{\circ}29'$
Ether, $\text{C}_4\text{H}_{10}\text{O}$ .....	74	$-1^{\circ}66'$
Hydrocyanic Acid, $\text{HCN}$ .....	27	$-1^{\circ}94'$

By means of this law the combining weights of compounds can be determined. Thus, analysis of lactic acid leads to the formula  $\text{CH}_2\text{O}$ , as expressing its composition. But, it has been found that three times the weight (in grams) indicated by this formula dissolved in 1000 grams

\* Ostwald's Lehrbuch der Allgemeine Chemie, Vol. I., p. 415.

of water lowers the freezing point of water to  $-1.92^{\circ}$ . The combining weight of lactic acid is then indicated by the formula  $C_3H_6O_3$ .

9. **Van t'Hoff's Law.**—When a volatile substance is passed up into the vacuum of a barometer, the vapour which escapes into the vacuum exerts a pressure upon the mercury and pushes it down a certain distance. If the temperature is raised, more vapour is formed and the vapour is expanded by the heat, both effects combining to depress the mercury still further. When the temperature is raised to the boiling point of the substance, the mercury sinks to the same level as that in the trough, showing that the pressure inside the tube equals that of the atmosphere\*. For any given temperature, the vapour of a volatile substance exerts in this way a certain pressure, known as its *vapour tension* and usually measured in millimetres of mercury. For example, the vapour tension of water at  $0^{\circ}\text{C}$  is 4.569; *i.e.* if water be passed up into a barometer tube kept at  $0^{\circ}\text{C}$ , the vapour from it will depress the mercury 4.569mm. The vapour tension of water at  $100^{\circ}\text{C}$  is 760, *i.e.* equal to the normal pressure of the atmosphere. The presence of dissolved substances decreases the vapour tension of the solvent, and according to a law precisely like that of Raoult just mentioned. *If weights proportional to the combining weights of compounds are dissolved in equal quantities of a solvent, the vapour tension of the solvent is lowered by approximately the same amount.* As in the case of Raoult's law, this applies only to dilute solutions. It is plain that it can be used for determining combining weights.

\*This is true only when some of the substance remains unvolatilised up to this point.